

A structural path for the icosahedra \leftrightarrow fcc structural transition in clusters

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We propose a structural path for the icosahedra \leftrightarrow fcc transition in clusters and demonstrate the transition in Pb_{13} by *ab initio* molecular-dynamics simulation. The proposed path can be described by using only two variables. The energy surface on this two-dimensional space for Pb_{13} was calculated and a barrierless fcc-to-ico energy path was found. The atomic displacements of the proposed structural transition for ico and fcc Pb_{13} were identified as one of the vibrational eigenmodes of the clusters with a soft mode for fcc Pb_{13} . These agree with the energy curvatures around the two structures, i.e. the ico Pb_{13} is at the bottom of a valley on the energy surface while the fcc Pb_{13} is at a saddle point. The barriers of this transition for larger clusters of Pb_n ($n=55$, 147 and 309) were also calculated, by *ab initio* elastic-band method, and found being smaller than the room-temperature thermal energy.

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Clusters can have a structure that is prohibited in the crystallographic translational-symmetry rules, e.g. the icosahedra (ico) and decahedra (deca) with non-crystalline fivefold symmetry. Nanoparticles of elements having fcc bulk structure have been observed to have structures with fivefold symmetry; the most studied ones include some metallic and rare-gas clusters[1]. As the growth of clusters proceeds beyond a crossover point, a structural transition to the crystalline structures is expected to take place. Experimentally it has been observed that structural transitions in clusters depend on the sizes of clusters as well as temperature[2]. A simple model for the ico \leftrightarrow deca transition, i.e. from one fivefold-symmetry cluster to another fivefold-symmetry cluster, has been proposed which involves a cooperative slip dislocation[2, 3]. However no microscopic model, to our knowledge, has ever been proposed for the transitions between the fivefold-symmetry ico and the crystalline structure of fcc cuboctahedra (fcc) of the same size. This transition can be a crucial process near the crossover point from clusters to the crystalline structure. In this Letter, we present a structural model for the ico \leftrightarrow fcc transition in clusters and perform *ab initio* molecular-dynamics (MD) calculations to demonstrate that a transition of fcc-to-ico following the proposed path indeed takes place in Pb_{13} .

The proposed model of the ico \leftrightarrow fcc transition for 13-atom and 55-atom clusters is schematically illustrated in Fig. 1(a) and 1(b). The most left panels show the ico structures with I_h symmetry and the most right panels are the fcc structures with O_h symmetry. Since these structures are highly symmetrical, all atoms except the center one can be separated into groups of atoms connected by symmetry operations and thus the complexity

of structural transition under high symmetry constraint can be greatly reduced. In fact by keeping the cluster within the T_h symmetry (the common subgroup of I_h and O_h), the cluster can easily transform between the icosahedra (I_h symmetry) and the fcc (O_h symmetry) structures (see Fig. 1). Specifically for the 13 atom-cluster, it can be viewed as one atom moving in a two-dimensional (2D) symmetry plane and only two variables are needed to describe the cluster. The first variable r is the interatomic distance of the outer atoms to the center atom. The second variable s describes the angular part ($\Theta = \tan^{-1} \sqrt{(2-s)/(2+s)}$) of the outer atom in the 2D plane. It is easy to verify that if the value of s equals to $\pm\sqrt{0.8}$, then the structure is ico; and the structure is fcc if s equals to 0. When the s variable changes from $\pm\sqrt{0.8}$ to 0, the cluster undergoes the ico-to-fcc transition as shown in Fig. 1(a).

The proposed description of the ico \leftrightarrow fcc transition can be observed in Pb_{13} by *ab initio* MD simulations. All electronic calculations in this study are based on the density functional theory[4] with the proposed generalized gradient approximation (GGA) by Perdew, Burke, and Ernzerhof[5] for the non-local correction to a purely local treatment of the exchange-correlation potential and energy. The single-particle Kohn-Sham equations[6] are solved using the plane-wave-based Vienna *ab-initio* simulation program (VASP) developed at the Institut für Material Physik of the Universität Wien [7]. The interactions between the ions and valence electrons are described by the projector augmented-wave (PAW) method[8] in the implementation of Kresse and Joubert[9]. The numbers of treated valence electrons are 4 and 3 for Pb and Al atoms respectively, we shall discuss the Al clusters later in the Letter. The energy cutoffs for the plane-

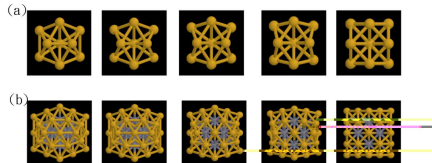


FIG. 1: The structural transition from ico (the most left panel) to fcc (the most right panel) in (a) 13-atom and (b) 55-atom clusters following the change of variable s as described in the text.

wave basis are 100eV and 241eV for Pb and Al systems respectively. All clusters were simulated by being placed in the center of cubic supercells which are large enough to neglect cluster-cluster interactions, i.e. a spacing of at least 10\AA separated by vacuum between the atoms of neighbouring clusters was used in the simulations. As the supercells are at least 14\AA in length, and going up to 38.4\AA for Pb_{309} , only one k point at the gamma point is included in the Brillouin-zone integration. Relaxation processes in optimizing static structures are accomplished by moving atoms to the positions at which all atomic forces are smaller than 0.02 eV/\AA . The molecular dynamics of the system was simulated by the canonical Nosé dynamics[10] with fictitious mass of 2 (in amu) and at least 10000 time steps of step size 1-femosecond.

In the static calculations of Pb_{13} , the ico structure was found more stable than the fcc structure by 2.24 eV (per cluster). Starting with the fcc structure of Pb_{13} we performed a few *ab initio* MD simulations of the system at various temperatures. The initial configurations of the MD simulations were taken as the static fcc Pb_{13} plus the randomly set atomic velocities according to the Maxwell-Boltzmann distribution at the temperatures of 50K, 100K, 300K and 500K. In all cases the fcc-to-ico transition, which followed the proposed path we described, was observed in the beginning of the simulation and succeeded by thermal vibrations about the ico structure. That the fcc-to-ico transition takes place in the beginning of the MD simulations for all the temperatures we studied suggests a barrierless transition in Pb_{13} . To verify this point, the energy surface of Pb_{13} on the 2D space of the transition variable s and the interatomic distance r was calculated and the result presented in Fig. 2. The electronic energy of a total of 169 structures on

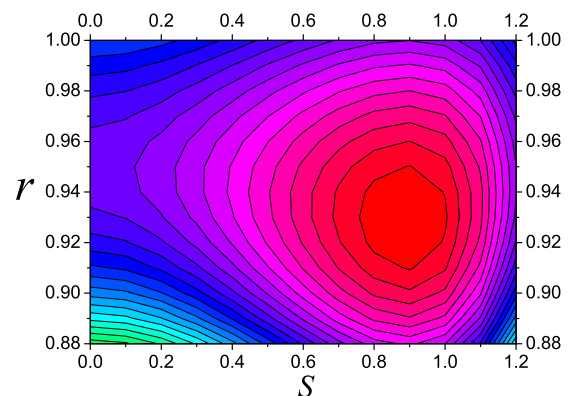


FIG. 2: The calculated energy surface of Pb_{13} in the 2D space of the variable s and the interatomic distance r . The spacing between the energy contours is 0.2 eV per cluster.

this 2D space were evaluated, i.e. 13 values of the variable s ranging from 0.0 to 1.2 and 13 values for the interatomic distance r ranging from 0.88 to 1.00 (in unit of the nearest-neighbour distance in bulk Pb) were considered. The ico Pb_{13} is at the bottom of the energy surface while the fcc Pb_{13} is at a saddle point. According to this 2D energy surface, the fcc-to-ico transition in Pb_{13} is indeed barrierless, as implied in the MD simulation. The energy space of a 13-atom cluster of course consists of many more degrees of freedom than two. In fact it consists of 33 degrees of freedom. However, we have demonstrated by *ab initio* MD simulations that the fcc-to-ico transition in Pb_{13} does follow the proposed transition path, though its 33-dimensional energy surface can in principle be very complicated.

TABLE I: The relative energies in the fcc and ico structures for Pb_n clusters and the energy barriers of the transition through the variable s transition path. The unit is in eV per cluster except the last line.

| n in Pb_n | 13 | 55 | 147 | 309 |
|-----------------|-----|--------|--------|--------|
| ico | 0.0 | 0.7 | 0.0 | 0.3 |
| fcc | 2.2 | 0.0 | 3.2 | 0.0 |
| barrier | 0.0 | 0.1 | 0.3 | 1.5 |
| barrier (eV/Pb) | 0.0 | 0.0018 | 0.0020 | 0.0049 |

It is expected that, when the transition approaching either terminal structure, the atomic displacements should be able to be described by an eigenmode of vibration or a linear combination of eigenmodes of the terminal structures. We have calculated the vibrational frequencies of the ico and fcc Pb_{13} through the Hessian matrix as provided in VASP. The atomic displacements of one of the vibrational eigenmodes of the ico and fcc Pb_{13} were found to be identical with the proposed description of transition. The eigenfrequencies are 1.82 (real value) and 1.30 (imaginary value) THz for the ico and fcc Pb_{13} respectively. The soft mode (imaginary frequency) corresponds to the negative curvature of the energy curve along the transition path at the fcc Pb_{13} as shown in Fig. 2. This is the only soft mode found in fcc Pb_{13} . That all the vibrational frequencies obtained for the ico Pb_{13} are real indicates ico Pb_{13} is a stable structure and on the 2D energy surface it is at the bottom of a valley.

This description of ico \leftrightarrow fcc transition can in general be applied to the clusters of larger sizes, for example see Fig. 1(b) for 55-atom cluster. One thing worth to mention here is that the proposed transition is a non-diffusive process. As the fcc-to-ico transition in Pb_{13} is barrierless, it will be interesting to know what the barriers are for the larger Pb clusters. The results of our studies for larger Pb_n clusters, including $n=55$, 147 and 309, are summarized in Table I. Firstly one notices that the relative stability actually oscillates as the cluster size increases. However, we should make clear that the comparison here is only for the two structures studied here, i.e. fcc and ico. Another high-symmetry cluster which is frequently considered in the studies of clusters is the deca structure. Our calculations show that the deca structure is the lowest energy state of the three high-symmetry structures of ico, fcc, and deca in Pb_{55} , the highest in Pb_{309} , and in the middle of ico and fcc in Pb_{13} and Pb_{147} . The barriers for the ico \leftrightarrow fcc transition were obtained from the elastic-band method with 8 configurations between the terminal structures of ico and fcc. The initial atomic structures for these 8 configurations were constructed from the structures of the corresponding variable s as well as the linear scaling of the bond lengths between the ico and fcc structures. Note that the barriers described here are the ones from the higher energy state to the lower one, i.e. it is the barrier of the ico-to-fcc transition in Pb_{55} and Pb_{309} but the fcc-to-ico

transition in Pb_{13} and Pb_{147} . Once a close-shelled structure, e.g. ico of Pb_{13} , is formed, a larger close-shelled structure, e.g. ico of Pb_{55} , can be easily grown by adding atoms to the smaller one, in spite of the fact that ico is less stable than fcc in Pb_{55} . Then the barrier needed to be overcome for the transition from ico to the more stable fcc in Pb_{55} is the barrier we discuss here. According to Table I, the energy barrier increases as the size of the cluster increases. We have also listed the energy barriers in terms of energy per atom which are all considerably smaller than the classical room-temperature thermal energy. Transitions from the less stable structure to the more stable one through the proposed path are therefore likely to occur at low temperature. The barriers for the reversed processes can be easily evaluated from adding the energy differences, as provided in the Table I, to the above discussed barriers. They are either smaller than or in the order of the room-temperature thermal energy which implies easy exchange in structures of these clusters at room temperature.

In case the symmetry of the cluster is broken, description of the proposed transition model requires more than two variables as the values of r and s are no longer identical for all the atoms (except the center one) in the cluster. Al_{13} is well-known to have a distorted ico structure[11]. The fcc Al_{13} is higher in electronic energy than the distorted ico Al_{13} by 0.9 eV (per cluster) in our calculations and the distorted ico is 0.1 eV lower in energy than the undistorted one. We have performed *ab initio* MD calculations for Al_{13} , similarly as we did for Pb_{13} , and the transition, roughly following the variable s , was also observed. The proposed path for the ico \leftrightarrow fcc transition is therefore not strictly confined to the transition between the symmetry group of the ico and fcc. For clusters of sizes larger than 13 atoms, the number of variables are more than two even when the symmetry of the cluster is not broken, e.g. the different interatomic distances between atoms belonging to different shells. In these systems, the transition can still possibly follow the proposed path. We have applied the embeded-atom-method MD to the Pd_{309} clusters and the fcc-to-ico transition through the proposed path was also observed.

In conclusion, we have proposed a variable- s description for the structural transition between the fivefold-symmetry ico structure and the fcc crystalline structure in clusters and demonstrated, using *ab initio* MD simulation, that in Pb_{13} the fcc-to-ico transition did follow this description. We have calculated the energy surface of the transition in Pb_{13} which shows the transition is barrierless. The atomic displacements of the structural transition in the fcc and ico Pb_{13} coincide with one of their vibrational eigenmodes with real and imaginary frequencies respectively. The barriers of the proposed transition path for Pb_n ($n=55$, 147, and 309) were evaluated and found to be smaller than the room-temperature thermal energy. The current results have provided a clear-cut microscopic structural model how the clusters evolve from non-crystalline motifs (ico)

to crystalline structures (fcc).

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